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None

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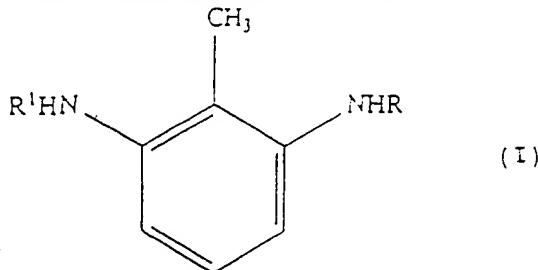
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(54) Substituted 2,6-diaminotoluenes useful in colouring agents

(57) Substituted 2,6-diaminotoluenes of the general formula



wherein either R denotes a hydrogen atom and

R¹ denotes a radical of general formula Ia

-CH<sub>2</sub>-CH(A)-B (Ia)

or R and R¹ independently denote a radical of general formula Ia, wherein if A in general formula Ia represents a hydrogen atom, B is a hydroxyl group or HO-CH<sub>2</sub>-group; and if A denotes a methyl group, B is a hydroxyl group, which are novel with the exception of N-(2-hydroxyethyl)-2,6-tolylendiamine, and salts thereof are useful in colouring agents, e.g. for dyeing hair.

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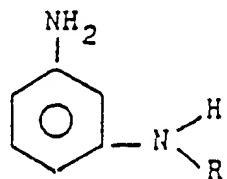
Substituted 2,6-diaminotoluenes

The invention relates to new substituted 2,6-diaminotoluenes of the general formula I, processes for their preparation, and colouring agents, particularly, but not exclusively, for keratinic fibres, which comprise these compounds.

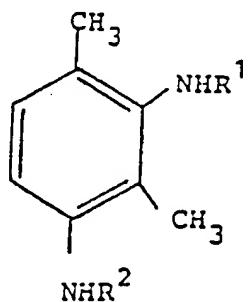
So-called oxidation dyes which are formed by oxidative coupling of development components (such as, for example, p-phenylenediamines, p-aminophenols or p-diaminopyridines) with coupling components (such as, for example, phenols, resorcinols, m-aminophenols, m-phenylenediamines, naphthols or pyrazolones) are of particular importance for dyeing hair. Under the conditions of use applicable to dyeing hair (low dyeing temperature and short dyeing time), they produce intensive colours with very good fastness properties. Oxidation dyes also play an important role in dyeing fur. Suitable oxidation dyestuff precursors must primarily meet the following requirements for use: during oxidative coupling with the particular coupling and development components, they must produce the desired colour, which should have a good absorption and migrating capacity on hair or fur, to an adequate intensity. The dyestuffs formed must be generally stable and specifically fast to washing, fast to light, fast to perspiration and heat stable. In particular, they should not lead to shifts in the colour of the original shade under wearing conditions. Moreover, they should be toxicologically and dermatologically acceptable.

These requirements cannot always be made to coincide. This is particularly clear in the field of so-called blue couplers. For example, 2,6-diaminotoluene is a compound which on the one hand is not completely satisfactory during use, since the stability of the colour of the dyed hair is not satisfactory, for example under the action of perspiration, acid rain, detergents, sunlight, UV radiation and the like, and may also be problematic from the toxicological point of view.

JP 51-12 41 94 A (1976) designates the compound N-(2-hydroxyethyl)-2,6-tolylendiamine, which is caused to react with maleic anhydride to polyimide resins. DE 30 45 959 A1 describes the use of N-hydroxyalkyl-substituted m-phenylenediamines of the general formula



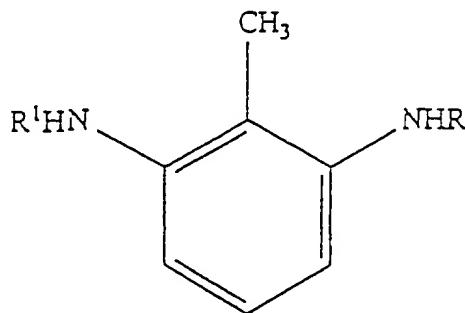
wherein R denotes a hydroxyalkyl radical with 1-4 carbon atoms and 1 or 2 hydroxyl groups as coupler component in agents for oxidative dying of hair to receive green till black-blue colour shades. DE 24 29 101 A1 shows in the example 4 the preparation of 2-hydroxyethylamino-4-aminotoluene and dying tests of this compound in combination with p-phenylenediamine or p-toluenediaminesulfate in agents for oxidative dying of hair. Deep blue colour shades are the result of this example. In DE-31 473 A1 is referred to 2,4-diamino-m-xylene of the general formula



in which one of the both substituents  $\text{R}^1$  or  $\text{R}^2$  is a hydrogen atom and the other substituent denotes a alkylgroup with 1-4 carbon atoms or a substituted alkylgroup. These compounds should give in agents for oxidative dyeing of hair green-grey, red-brown, black-blue or dark-violet shades.

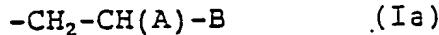
We have now found it possible to improve the previous disadvantages of hair colouring agents based on an oxidative method. In particular, we have found it possible to produce dyed keratin fibres which are stable, bright and intense in colour, and thus have significantly improved properties in respect of attack by perspiration, acid rain, detergents, sunlight, UV radiation and the like.

According to one aspect of the present invention there is provided a 2,6-diaminotoluene derivative of general formula I and salts thereof with inorganic and organic acids



(I)

wherein either R denotes a hydrogen atom and  
 $R^1$  denotes a radical of general formula Ia

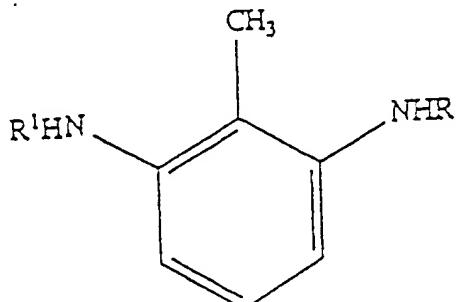


or R and  $R^1$  independently denote a radical of general formula Ia, wherein if A in general formula Ia represents a hydrogen atom, B is a hydroxyl group or  $HO-CH_2-$  group; and if A denotes a methyl group, B is a hydroxyl group; with the proviso that the derivative is not N-(2-hydroxyethyl)-2,6-toluenediamine.

Preferably the compound is

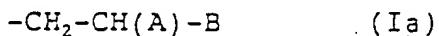
2,6-Bis(2-hydroxyethylamino)-toluene.

According to another aspect of the present invention there is provided a process for the preparation of a compound of general formula I' and salts thereof with inorganic and organic acids



(I')

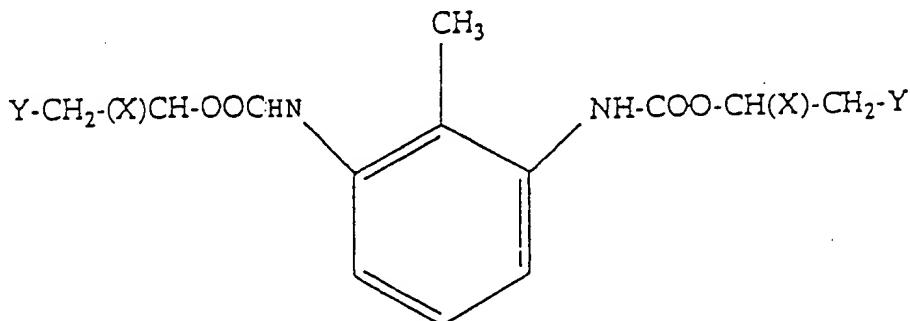
wherein  $\text{R}$  denotes a hydrogen atom and  $\text{R}^1$  denotes a radical of general formula Ia



or  $\text{R}$  and  $\text{R}^1$  independently denote a radical of general formula Ia, wherein if A in general formula Ia represents a hydrogen atom, B is a hydroxyl group or  $\text{HO}-\text{CH}_2-$  group; and if A denotes a methyl group, B is a hydroxyl group,

wherein either

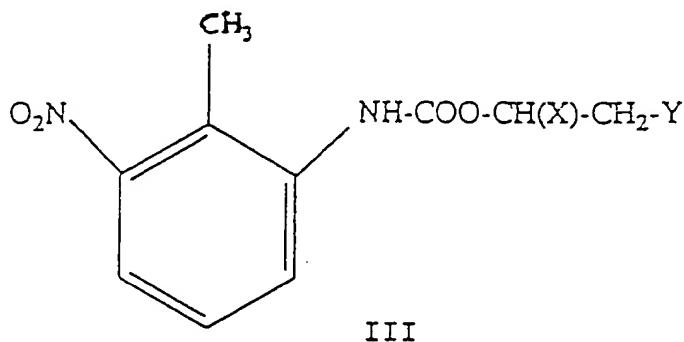
a.) 2,6-diaminotoluene is reacted with a chloroformic acid alkyl ester of general formula  $\text{Cl}-\text{COO}-\text{CH}(\text{X})-\text{CH}_2-\text{Y}$ , wherein  $\text{X}=\text{H}$ ,  $\text{Y}=\text{Cl}$ ;  $\text{X}=\text{CH}_2$ ,  $\text{Y}=\text{Cl}$  or  $\text{X}=\text{H}$ ,  $\text{Y}=\text{CH}_2\text{Cl}$ , to give a carbamate of the general formula II



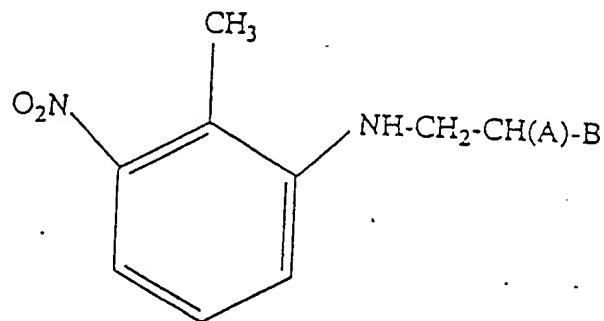
II

wherein X and Y are as previously defined, and converting the carbamate of general formula II into the compound of the general formula I', wherein R and R<sup>1</sup> denote a radical of general formula Ia, wherein A and B are as previously defined, or

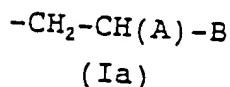
b.) 2-nitro-6-aminotoluene is reacted with a chloroformic acid alkyl ester of general formula C1-COO-CH(X)-CH<sub>2</sub>-Y, wherein X and Y are as previously defined, to give a carbamate of general formula III



wherein X and Y are as previously defined, and converting the carbamate of general formula III into a compound of general formula IV



wherein A and B are as previously defined and reducing the compound of general formula IV; and, if appropriate, converting the resulting compound of general formula I', wherein one of R or R<sup>1</sup> denotes a hydrogen atom or R and/or R<sup>1</sup> denotes a radical of general formula Ia



wherein A and B are as previously defined into a salt thereof with an organic or inorganic acid.

The compounds of the general formula I', which are particularly suitable as coupler components for oxidative dyeing, meet the abovementioned requirements to a high degree. They form intensive brown, blonde, violet and blue shades of high heat stability and fastness to light with a large number of the known developer substances. The compatibility of compounds of the general formula I' with further couplers and direct dyestuffs is very good, and controlled modification of the shades of known developer/coupler systems are therefore also possible. They can be prepared according to the invention economically and in a high purity and yield from commercially obtainable precursors.

The new coupler compounds of the general formula I wherein R and R<sup>1</sup> have the meanings given above are therefore a valuable enrichment of the range of oxidation hair dyestuff precursors. (see Table I)

Preferred embodiment and features of the process according to the invention are described below. (see Table I')

In carrying out the process mentioned under a), 2,6-diaminotoluene may initially be introduced into the

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Table I

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The general formula I includes the following substituents:

15

	R	R <sup>1</sup>
15	H	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
	H	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
20	-CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH <sub>2</sub> -OH
	-CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
	-CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
25	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
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Table I'

The general formula I' includes the following substituents:

	R	R <sup>1</sup>
10		
15	H	-CH <sub>2</sub> -CH <sub>2</sub> -OH
20	H	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
	H	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
25	-CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH <sub>2</sub> -OH
	-CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
	-CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
30	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH
	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH
	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH	-CH <sub>2</sub> -CH(CH <sub>3</sub> )-OH

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reaction vessel in an inert organic solvent, such as, for example, dioxane, C<sub>1</sub>- to C<sub>4</sub>-alcohol, dimethylformamide, tetrahydrofuran, toluene, chlorobenzene, methyl ethyl ketone, ethylene glycol dimethyl ether or diethylene glycol dimethyl ether, and is heated up to a temperature between room temperature and the reflux temperature, preferably between 70°C and the reflux temperature. Preferably, the molar amount of a chloroformic acid alkyl ester of the general formula Cl-COO-CH(X)-CH<sub>2</sub>-Y, wherein X=H, Y=Cl; 5 X=CH<sub>3</sub>, Y=Cl; or X=H, Y=CH<sub>2</sub>Cl, may then be metered in. If appropriate, the solvents can be combined with water. An acid-binding agent can either be initially introduced at the same time or added in parallel with the chloroformic acid chloroalkyl ester already mentioned. Possible acid-binding agents are bases, such as alkali metal hydroxides, bicarbonates and carbonates, alkaline earth metal oxides, hydroxides, bicarbonates and carbonates, and tertiary organic amines. The reaction is generally complete after about 2 - 8 hours. For working up, it is possible either 10 to add water and to stir the mixture until cold, or to filter off the inorganic salts and distil off some or all 15 of the solvent.

20

To form the compounds of general formula I wherein R and R' represents a radical of general 25 formula Ia, the carbamates of the general formula II may be treated with strong bases (alkali metal hydroxides or alkaline earth metal hydroxides), preferably with 10 - 50% strength sodium or potassium hydroxide solution. The carbamate of formula II is preferably initially introduced into 30 the reaction vessel in water or an organic solvent, such as, for example, a (C<sub>1</sub>-C<sub>4</sub>)-alcohol, a water-miscible ether or mixtures thereof, and about 6 mol of alkali per mol of carbamate are then metered in at room temperature. It is also possible for the alkali, which can be diluted with 35 the solvents mentioned, to be initially introduced into the reaction vessel and for the carbamate to be metered into the alkali in the pure form or as a solution in one of the organic solvents mentioned. The mixture is then

subsequently stirred, for complete reaction, and if appropriate it can be heated under reflux. The reaction time is generally about 2 to 10 hours. For working up, the reaction solution, which has a pH of about 12 - 14, may be neutralised to a pH of about 7 to 10 with an organic or inorganic acid. Water is then added, if appropriate the solvents are distilled off, and the product is isolated.

In carrying out the process mentioned under b), 2-nitro-6-aminotoluene is used as the starting substance. The 2-nitro-6-aminotoluene is reacted with preferably one mol of chloroformic acid chloroalkyl ester of the general formula  $\text{Cl}-\text{COO}-\text{CH}(\text{X})-\text{CH}_2-\text{Y}$ , wherein  $\text{X}=\text{H}$ ,  $\text{Y}=\text{Cl}$ ;  $\text{X}=\text{CH}_3$ ,  $\text{Y}=\text{Cl}$ ; or  $\text{X}=\text{H}$ ,  $\text{Y}=\text{CH}_2\text{Cl}$ , in a solvent as mentioned under a). under the conditions mentioned there. The carbamates of general formula III thus obtained may be treated with strong bases (alkali metal hydroxides or alkaline earth metal hydroxides), preferably with 10 - 50% strength sodium or potassium hydroxide solution. The carbamate of formula II is preferably initially introduced into the reaction vessel in water or an organic solvent, such as, for example, a ( $\text{C}_1-\text{C}_4$ )-alcohol, a water-miscible ether or mixtures thereof, and about 3 mol of alkali per mol of carbamate are then added at room temperature. It is also possible for the alkali, which can be diluted with the solvents mentioned, to be initially introduced and for the carbamate to be metered into the alkali in the pure form or as a solution in one of the organic solvents mentioned. The mixture is then subsequently stirred for complete reaction, and if appropriate it can be heated under reflux. The reaction time is generally about 2 to 8 hours. For working up, the reaction solution, which has a pH of about 12 - 14, may be neutralised to a pH of about 7 to 10 with an organic or inorganic acid. Water is then added, if appropriate the solvents are distilled off, and the product is isolated.

The compounds of general formula I' wherein R denotes a radical of general formula Ia and  $\text{R}' = \text{H}$  or  $\text{R}'$  represents a radical of general formula Ia and  $\text{R}=\text{H}$

can be prepared by reduction of the compounds of the general formula IV preferably with base metals or by catalytic reduction.

Customary catalysts, such as, for example, Raney nickel, palladium-on-active charcoal or platinum-on-active charcoal, may be employed for catalytic reduction with hydrogen. The reaction temperature may be between room temperature and 120°C, preferably between 40 and 80°C, and the pressure is between normal pressure and 100 bar, preferably between 20 and 80 bar. The solvents which may be used are the customary solvents, such as water, toluene, glacial acetic acid, lower alcohols and ethers. When the reduction has been carried out and the catalyst has been removed, the product of the general formula I can be isolated in the free form by stripping off the solvent under an inert gas, but it is preferably converted into a salt - also under an inert gas - by addition of approximately the equivalent amount of an acid, the salt either precipitating directly or being obtained after stripping off the solvent. Suitable inorganic acids for the salt formation are, for example, hydrochloric acid and phosphoric acid, and suitable organic acids for the salt formation are, for example, acetic acid, propionic acid, lactic acid or citric acid.

The preparation process is illustrated by the following non-limiting examples:

Example 1

Preparation of 2,6-bis(β-hydroxyethylamino)toluene

1st stage : Preparation of 2,6-bis-(β-chloroethoxycarbonylamino)-toluene

122 g of diaminotoluene and 105 g of calcium carbonate are initially introduced into 500 ml of monoethylene glycol dimethyl ether, and the mixture is heated to 78°C, while stirring. 300 g of β-chloroethylchloroformate are metered in to the mixture in the course of 30 minutes, and the mixture is subsequently stirred at 80°C for 3 hours. 500 g of ice and 500 g of water are then added to the mixture, and the product which has precipitated

is filtered off, rinsed twice with 100 ml of water each time and dried at 80°C in a vacuum drying cabinet.

Yield: 301.5 g (90% of the theoretical yield)

Melting point: 148 - 149°C

5      2nd stage : Preparation of 2,6-bis(β-hydroxyethylamino)toluene

33.5 g of the 2,6-bis-(β-chloroethoxycarbamoyl-amino)-toluene obtained above under the 1st stage are initially introduced into the reaction vessel in 200 ml of water and 30 ml of methanol. The reaction mixture is heated to 75°C, and 70 g of 50% strength potassium hydroxide solution are added dropwise in the course of one hour. After the mixture has been subsequently stirred at 60°C for 2½ hours, the pH is brought to 8.0 with glacial acetic acid and the reaction mixture is cooled slowly. The product which has precipitated is filtered off with suction, washed with water and dried at 50°C in a vacuum cabinet.

Yield: 18 g (86% of the theoretical value)

Melting point: 118 - 120°C

20     Example 2

1st stage : Preparation of 2,6-bis(γ-chloropropoxy carbonylamino)-toluene

61 g of 2,6-diaminotoluene and 52.5 g of calcium carbonate are reacted with 160 g of γ-chloropropylchloroformate in 250 ml of monoethylene glycol dimethyl ether under the conditions mentioned in Example 1, stage 1, and the mixture is worked up.

172 g (95% of the theoretical value) of 2,6-bis(γ-chloropropoxy carbonylamino)-toluene are obtained

30     2nd stage : Preparation of 2,6-bis(γ-hydroxypropylamino)-toluene

36.3 g of the 2,6-bis-(γ-chloropropoxy-carbonylamino)-toluene prepared above under Example 2, stage 1 are reacted with 70 g of 50% strength aqueous potassium hydroxide solution in 190 ml of water and 40 ml of ethanol under the conditions mentioned in Example 1, stage 2, and the mixture is worked up.

19 g (80% of the theoretical yield) of 2,6-bis(γ-hydroxypropylamino)-toluene are obtained.

Example 3

Preparation of 2-( $\beta$ -hydroxyethylamino)-6-aminotoluene

1st stage : Preparation of  $\beta$ -chloroethyl N-(2-methyl-3-nitrophenyl)-carbamate

5        91 g of 2-nitro-6-aminotoluene and 31 g of calcium carbonate are initially introduced into the reaction vessel in 750 ml of dioxane, and are heated up to 70°C. 87 g of  $\beta$ -chloroethyl chloroformate are added dropwise to this mixture in the course of two hours such  
10      that the reaction mixture refluxes gently, carbon dioxide being evolved. The mixture is subsequently stirred under reflux for a further two hours and then cooled to 35°C, and water and ice are added. The product which has precipitated is filtered off with suction, washed with  
15      water and dried.

Yield: 152 g (98% of the theoretical yield)

Melting point: 101 - 103°C

2nd stage : Preparation of 2-( $\beta$ -hydroxyethylamino)-6-nitrotoluene

20       25.8 g of the  $\beta$ -chloroethyl N-(2-methyl-3-nitrophenyl)-carbamate prepared under Example 3, stage 1, are initially introduced into the reaction vessel in 250 ml of water. The reaction mixture is heated to 80°C, and 35 g of 50% strength aqueous potassium hydroxide solution are then added in the course of one hour. After the  
25      mixture has been subsequently stirred at 75°C for 3 hours, its pH is brought to 8 with glacial acetic acid, and the reaction mixture is cooled slowly. The product which has precipitated is filtered off with suction, washed with water and dried at 50°C in a vacuum drying  
30      cabinet.

Yield: 16 g (82% of the theoretical value)

Melting point: 82 - 83°C

3rd stage : Preparation of 2-( $\beta$ -hydroxyethylamino)-6-aminotoluene

35       10 g of the 2-( $\beta$ -hydroxyethylamino)-6-nitrotoluene prepared under Example 3, stage 2 are transferred to a stainless steel autoclave together with 200 ml of methanol, about 2 g of Raney nickel are added and catalytic reduction is carried out with hydrogen under a

hydrogen pressure of 20 bar at 70°C in the course of 6 hours. After the catalyst has been removed, the mother liquor is concentrated, and the product is isolated and dried.

5 Yield. 7 g (85% of the theoretical yield)

Melting point: 97 - 99°C

The compounds of the present invention, particularly compounds of general formula I<sup>1</sup>, may be used as hair colouring agents, particularly as coupler components and developer substances generally used for oxidation hair dyeing, they are distinguished

10 by good storage stability and, when used, produce very intensive colour shades, which range from dark blonde to blue and have good fastness properties, of the dyeings achieved with them.

15 When used in hair colouring agents, the coupler components are in general employed in approximately molar amounts, based on the developer substances used. Although molar use proves to be advantageous, it is not a disadvantage if the coupler component is employed in a certain amount more or less than the molar amount.

20 The compounds of the general formula I to be used as coupler components can be employed either as such or in the form of their salts with inorganic or organic acids, such as, for example, as chlorides, sulphates, phosphates, acetates, propionates, lactates or citrates.

25 The hair colouring agents according to the invention should comprise the coupler substances or their salts in a concentration of about 0.001 to 5.0% by weight, in particular 0.2 to 3.0% by weight.

30 Furthermore, it is not necessary for only one developer component to be used, thus, it is also possible to use a mixture of different developer compounds.

35 Examples which may be mentioned of developer components to be employed are primary aromatic or heteroaromatic amines having another functional group in the p-position, such as p-phenylenediamine, p-toluylenediamine,

p-aminophenol, N,N-dimethyl-p-phenylenediamine, chloro-p-phenylenediamine, methoxy-p-phenylenediamine, 2,5-di-aminopyridine and its derivatives, and other compounds of this type, which additionally contain one or 5 more functional groups, such as OH groups, NH<sub>2</sub> groups, NHR groups or NRR groups, wherein R represents an optionally substituted alkyl radical having 1 to 4 carbon atoms.

It is furthermore not necessary for only the 10 coupler components of the general formula I' according to the invention to be used; rather, other coupler components which are already known and used, such as, for example,  $\alpha$ -naphthol, 3,4-diaminobenzoic acid, resorcinol, 4-chlororesorcinol, m-aminophenol, m-phenylenediamine, m-15 toluylenediamine, 2,4-diaminoanisole, pyrocatechol, pyrogallol, 1,5- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, 6-amino-2-methylphenol and derivatives of the compounds mentioned, can also be employed in order to achieve certain colour shades.

20 The hair colouring agents moreover can comprise customary direct dyestuffs, if this is necessary in order to achieve certain colour shades. Oxidative coupling, that is to say development of the dyeing, can in principle be effected by atmospheric oxygen, as is also the 25 case with other oxidation dyestuffs. However, chemical oxidising agents which are known to the expert are advantageously employed.

The hair colouring agents according to the invention may be in the form of aqueous compositions. By these, there 30 are understood all compositions which contain water in any manner, such as, for example, creams, emulsions, suspensions, gels or also simple solutions. The compositions of the hair colouring agents represent a mixture of the dyestuff components with additives customary for cosmetics formulations.

35 Customary additives in solutions, creams, emulsions or gels are, for example, solvents, such as water, lower aliphatic alcohols, for example ethanol, propanol and isopropanol, or glycols, such as glycerol, and glycol

ethers, such as propylene glycol, and furthermore wetting agents or emulsifiers selected from anionic, cationic, amphoteric or non-ionic surface-active substances, such as fatty alcohol sulphates, alkyl-  
5 sulphonates, alkylbenzenesulphonates, alkyltrimethyl-  
ammonium salts, alkylbetaines, oxyethylated fatty alcohols, oxyethylated nonylphenols, fatty acid alkanolamides and oxyethylated fatty acid esters, and furthermore thickeners, such as, for example, higher fatty alcohols,  
10 starch, cellulose derivatives, petroleum jelly, paraffin oil and fatty acids.

The constituents mentioned are used in the amounts customary for such purposes, for example the formulations may comprise wetting agents and emulsifiers in concentrations of about 0.5 to 30% by weight, while they may comprise thickeners in an amount of  
15 about 0.1 to 25% by weight.

The hair colouring agents according to the invention can be weakly acid, neutral or alkaline, depending on the composition. In general, they have a pH in the alkaline range of between 7.5 and 11.5, the pH preferably being established with ammonia. However, it is also possible to use organic amines, for example mono-ethanolamine and triethanolamine, or inorganic bases, such as sodium hydroxide and potassium hydroxide.  
25

In processes for oxidative dyeing of hair, a hair colouring composition of the invention, which comprises a combination of developer substances known in hair dyeing with at least one compound of general formula I' or I or salt thereof as the coupler substance, and if appropriate additionally known coupler substances and direct dyestuffs, may be mixed with an oxidising agent shortly before use, and this mixture is applied to the hair. Examples of oxidising agents for development of hair dyeing include  
30 hydrogen peroxide, for example as a 6% strength by weight aqueous solution, and addition compounds thereof on urea, melamine or sodium borate, as well as mixtures of  
35 hydrogen peroxide addition compounds with potassium

peroxodisulphate. Temperatures for use vary in the range from 15 to 40°C. After an action time of about 30 minutes, the hair colouring agent is removed by rinsing from the hair to be coloured. Thereafter, the hair is subsequently washed with a mild shampoo and dried.

5 The following non-limiting examples further illustrate the invention:

Example 4

10 *Hair colouring agent in cream form*

1.00 g of	2,6-bis(2-hydroxyethylamino)toluene
1.30 g of	p-phenylenediamine HCl
0.05 g of	m-phenylenediamine
2.00 g of	oleic acid
15 0.10 g of	polyacrylic acid
0.50 g of	sodium dithionite
4.00 g of	lauryl alcohol diglycol ether sulphate, sodium salt (28% strength solution)
15.0 g of	cetyl alcohol
20 8.00 g of	ammonia, 25%

Water to 100

25 50 g of the abovementioned hair colouring agent are mixed with 50 g of hydrogen peroxide solution, 6% strength by weight, shortly before use. The mixture is allowed to act on medium-brown natural hair having a 20% grey content at 38°C for 30 minutes. Thereafter, the hair colouring agent is rinsed out, and the hair is subsequently shampooed and dried.

30 The hair has been given an intensive aubergine shade.

Example 5

*Hair colouring agent in cream form*

0.70 g of	2-β-hydroxyethylaminoamino-6-aminotoluene
0.65 g of	p-aminotoluene
35 0.15 g of	a-naphthol (sic)
0.25 g of	HC Red No. 3
2.10 g of	oleic acid
0.12 g of	polyacrylic acid

0.50 g of sodium sulphite, anhydrous  
4.50 g of lauryl alcohol diglycol ether sulphate,  
sodium salt (28% strength solution)

16.0 g of cetyl alcohol  
5 8.00 g of ammonia, 25%

Water to 100

10 50 g of the abovementioned hair colouring agent are mixed with 50 g of hydrogen peroxide solution, 6% strength by weight, shortly before use. The mixture is allowed to act on dark blonde natural hair having a 30% grey content at 40°C for 35 minutes. Thereafter, the hair colouring agent is rinsed out, and the hair is subsequently shampooed and dried.

It has been given a strong red-violet shade.

15 Example 6

Hair colouring agent in gel form

0.28 g of 2,6-bis(2-hydroxyethylamino)toluene  
0.38 g of p-phenylenediamine HCl  
0.03 g of a-naphthol (sic)  
20 14.0 g of oleic acid  
10.0 g of isopropanol  
2.60 g of PEG 3-cocamine  
10.0 g of ammonia, 25%  
0.50 g of ascorbic acid  
25 Water to 100

30 40 g of the abovementioned colouring agent are mixed with 60 g of hydrogen peroxide solution, 6% strength by weight, shortly before use. The mixture is allowed to act on medium-blonde natural hair at 40°C for 30 minutes. Thereafter, the hair colouring agent is rinsed out, and the hair is subsequently shampooed and dried.

The hair has been coloured an intensive rosewood shade.

35 Example 7

Hair colouring agent in cream form

0.45 g of 2,6-bis(3-hydroxypropylamino)-toluene  
0.45 g of p-phenylenediamine HCl

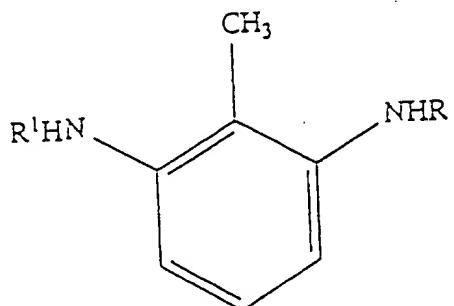
0.06 g of m-aminophenol  
0.45 g of HC Red No. 3  
2.00 g of oleic acid  
0.10 g of polyacrylic acid  
5 0.50 g of sodium sulphite, anhydrous  
4.00 g of lauryl alcohol diglycol ether sulphate,  
sodium salt (28% strength solution)  
15.0 g of cetyl alcohol  
8.00 g of ammonia, 25% strength  
10 Water to 100

50 g of the abovementioned colouring agent are mixed with 50 g of hydrogen peroxide solution, 6% strength by weight, shortly before use. The mixture is allowed to act on medium-blonde natural hair having a 30% grey content at 38°C for 30 minutes. Thereafter, the hair colouring agent is rinsed out, and the hair is subsequently shampooed and dried.

15 It has been given a strong red-violet shade.

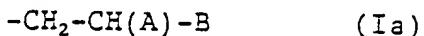
## **CLAIMS**

1. 2,6-Diaminotoluene derivative of general formula I and salts thereof with inorganic and organic acids



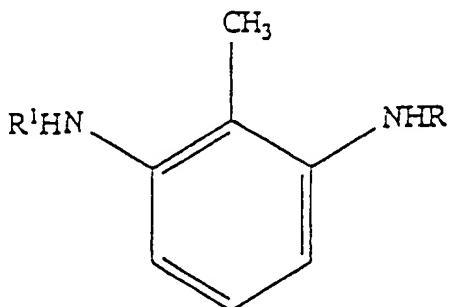
( I )

wherein either R denotes a hydrogen atom and R<sup>1</sup> denotes a radical of general formula Ia



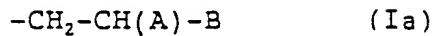
or R and R<sup>1</sup> independently denote a radical of general formula Ia, wherein if A in general formula Ia represents a hydrogen atom, B is a hydroxyl group or HO-CH<sub>2</sub>- group; and if A denotes a methyl group, B is a hydroxyl group; with the proviso that the derivative is not N-(2-hydroxyethyl)-2,6-tolylenediamine.

2. 2,6-Bis(2-hydroxyethylamino)-toluene.  
3. 2,6-Bis(3-hydroxypropylamino)-toluene.  
4. A process for the preparation of a compound of general formula I' and salts thereof with inorganic and organic acids



( 1 )

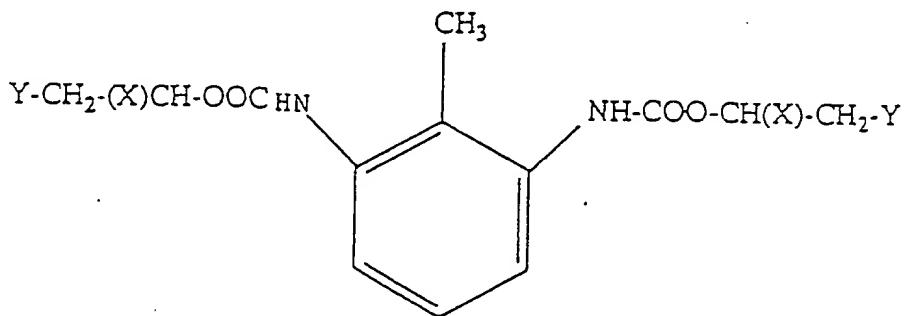
wherein R denotes a hydrogen atom and  
R<sup>1</sup> denotes a radical of general formula Ia



or R and R<sup>1</sup> independently denote a radical of general formula Ia,  
wherein if A in general formula Ia represents a hydrogen atom, B is a  
hydroxyl group or HO-CH<sub>2</sub>- group; and if A denotes a methyl group, B is  
a hydroxyl group,

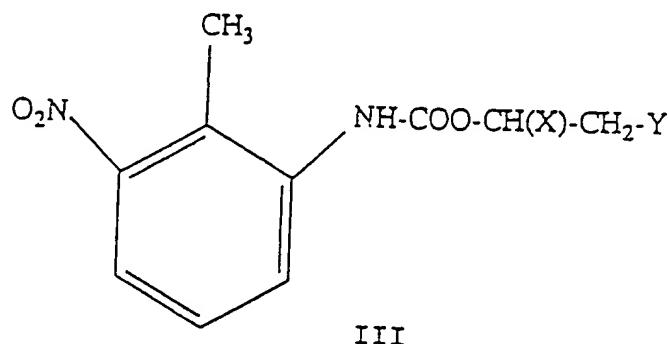
wherein either

a.) 2,6-diaminotoluene is reacted with a chloroformic acid alkyl ester of general formula Cl-COO-CH-CH<sub>2</sub>-Y, wherein X=H, Y=Cl; X=CH<sub>3</sub>, Y=Cl or X=H, Y=CH<sub>2</sub>Cl, to give a carbamate of the general formula II

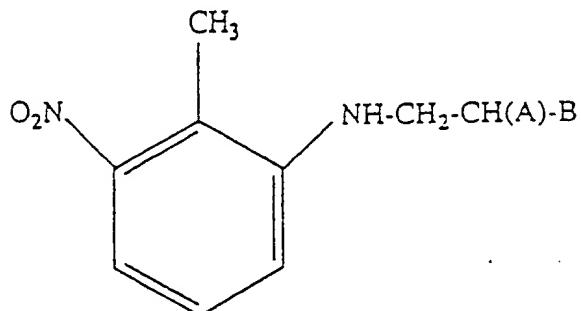


wherein X and Y are as previously defined, and converting the carbamate of general formula II into the compound of the general formula I', wherein R and R<sup>1</sup> denote a radical of general formula Ia, wherein A and B are as previously defined, or

b.) 2-nitro-6-aminotoluene is reacted with a chloroformic acid alkyl ester of general formula Cl-COO-CH(X)-CH<sub>2</sub>-Y, wherein X and Y are as previously defined, to give a carbamate of general formula III

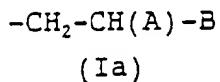


wherein X and Y are as previously defined, and converting the carbamate of general formula III into a compound of general formula IV



(IV)

wherein A and B are as previously defined and reducing the compound of general formula IV; and, if appropriate, converting the resulting compound of general formula I', wherein one of R or R' denotes a hydrogen atom or R and/or R' denotes a radical of general formula Ia,



wherein A and B are as previously defined, into a salt thereof with an organic or inorganic acid.

5. A process according to claim 4, wherein in a) 2,6-diaminotoluene is reacted with about twice the molar amount of the chloroformic acid alkyl ester.

6. A process according to either of claims 4 and 5, wherein in b) 2-nitro-6-aminotoluene is reacted with an approximately equimolar amount of the chloroformic acid alkyl acid.

7. A process according to any one of claims 4 to 6, wherein in b) the carbamate of general formula III is converted into a compound of general formula IV by treatment with a base.

8. An agent for oxidative dyeing of hair which is based on a developer-coupler combination, comprising at least one compound of the general formula I' as defined in claim 4 as the coupler component.

9. An agent according to claim 8, comprising at least one compound as defined in any one of claims 1 to 3.

10. An agent according to either of claims 8 and 9, wherein the compound is present in an amount of 0.001 to 5 per cent by weight of the total agent.

11. An agent according to any one of claims 8 to 10, comprising further development and/or coupling components as dyestuff precursors.

12. An agent according to any one of claims 8 to 11, comprising direct dyestuffs.

13. An agent according to any one of claims 8 to 12, wherein the pH of the agent is in the range of from about 6.0 to 12.5.

14. An agent according to claim 13, wherein the pH is in the range of from 7.5 to 11.5.

15. A process for the oxidative dyeing of hair, comprising applying an agent according to any one of claims 8 to 14 to hair.

16. A compound according to claim 1 as herein specifically disclosed.

17. A process according to claim 4 substantially as herein disclosed.

18. An agent according to claim 8 as herein specifically disclosed.

**Patents Act 1977****Examiner's report to the Comptroller under  
Section 17 (The Search Report)**

Application number

GB 9220658.0

**Relevant Technical fields**

(i) UK CI (Edition      K )      C2C CLE

(ii) Int CI (Edition      5      )      C07C

**Search Examiner**

P N DAVEY

**Databases (see over)**

(i) UK Patent Office

(ii)      ONLINE DATABASES : CAS ONLINE

**Date of Search**

22 OCTOBER 1992

Documents considered relevant following a search in respect of claims

1-18

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Category	Identity of document and relevant passages	Relevant to claim(s).

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